

THE APPLICATION OF INVERSE GAS CHROMATOGRAPHY TO COALS AND OXIDIZED COALS*

P. H. Neill and R. E. Winans
Chemistry Division, Argonne National Laboratory
9700 South Cass Avenue, Argonne Illinois 60439

Introduction

In a previous paper (1) we reported the preliminary results concerning the application of Inverse Gas Chromatography (IGC) to coals. This paper will cover the extension of the technique to coals of various ranks and degrees of air oxidation.

The objective of this study is to provide detailed information on possible changes in the chemical and physical structures of the Argonne Premium Coal Samples during storage. In meeting this objective, new fundamental data will be obtained on this unique set of coal samples. The use of a broad range of experiments is planned in this study, but only one approach will be described here. While it is known that subtle changes in the physical and chemical structure of bituminous coals can effect changes in the plasticity upon heating, the techniques traditionally used to measure plasticity do not yield information which can be used to understand these changes.

A new approach, inverse gas chromatography (IGC), a technique widely used for studying polymers, is being used to study phase transitions in coals upon heating. Inverse GC has been applied to polymers to measure the glass transition temperature, the degree of crystallinity, melting point, thermodynamics of solution, and chemical composition (2-4). In contrast to classical GC, inverse chromatography probes the stationary phase, a coal, by determining the retention time of known compounds on it. This transposition of known and unknown in the GC experiment gives rise to the term "inverse chromatography". The coal samples will be chosen to examine variations with rank and to investigate structural changes in ground coals, both in air and in the absence of air, as a function of time. These approaches show promise for providing chemical information on subtle variations in coal structure.

Experimental

The coals used in this study included an Illinois No. 2 hvC bituminous, an Upper Freeport mv bituminous which is, an Argonne Premium Coal Sample, and a Bruceton hvA bituminous. The elemental compositions are shown in Table 1. The Illinois No. 2 was ground to -100 mesh and soxhlet extracted with an azeotropic mixture of benzene and ethanol, and dried under vacuum at 110°C. The other two fresh coals were used as received. The oxidized Upper Freeport was exposed to air in an oven at 100°C for 90 hrs. The coals were thoroughly mixed with non-porous glass beads (-40 to -60 mesh) to give a mixture approximately 10% coal on a weight basis. The six foot by 1/4" glass columns were packed with ca. 30 grams of the mixture.

*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-31-109-ENG-38. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

The GC equipped with a single FID could be controlled, within one degree C, from an external computer. The injector was a computer controlled Carle gas sampling valve in a thermostated box. Flow control was provided by two flow controllers one with a 0-5 ml/min. element and the second with a 0-60 ml/min. element. The 0-60 ml/min. controller was connected to the injector through a computer controlled solenoid. The experiment was controlled and the data analyzed by a IBM PC computer. The probe, methane, was injected onto the column and its retention time at the specific temperature was determined. In the experiment chromatograms were obtained in three degree increments between 50 and 450°C. The injector was held at 100°C and the detector at 400°C.

Results and Discussion

The retention volume may be related, through the partition coefficient, to the free energy or enthalpy of adsorption, and a plot of $\ln t_{\text{ret}}$ vs. $1/T$ gives a slope proportional to ΔH_s . Changes in the thermodynamics of retention result in discontinuities or changes in the slope of the plot. Plots of the three unoxidized coals are presented in Figure 1, with temperatures of significant transitions given in Table 2. They do not appear to vary greatly in an overall gross sense. Each has what appears to be a transition at relatively low temperatures as illustrated by T_A in the figure. This transition is most likely due to the loss of water from the surface and from the pores of the coal. The second region of interest is at T_B . This dip in the otherwise smooth portion of the curves can be attributed to the loss of chemical water. This transition varies in temperature with the coal, however there does not appear to be a rank dependence. The Bruceton coal seems to loose its water at the lowest temperature while the Upper Freeport at the highest.

At T_C a number of small transitions begin to occur for each of the coals. This is also the region where relatively large amounts of volatile material is beginning to be released. Due to the small thermodynamic changes in the interaction between the probe and the coal it is difficult to assign a starting temperature for this region, however it does appear to begin at a higher temperature for the Upper Freeport mv coal than the Bruceton hvA coal. Comparisons between the Illinois No. 2 hvC coal and the others would be speculative since this coal was pre-extracted. Thus, a large percentage of the volatile matter has been removed.

The primary transition in the plots occurs at T_P . In each case there is a marked increase in the retention time followed by a rapid decrease. This transition correlates well with the onset of plasticity in each of the coals, occurring 10 to 15°C before the initial softening temperature. The temperature at which the major transition occurs is also correlated with rank. The Illinois No. 2 exhibits the transition at a lower temperature, followed by the Bruceton and the Upper Freeport. The Bruceton hvC coal is the only one that appeared to have a leveling off of the slope of the curve by T_P . The Giesler plasticity measurement shows that this coal resolidifies just above the maximum temperature of this experiment. Thus, it appears that some of the post fluid pore structure has appeared and is showing up in the IGC data.

Figure 2 illustrates the effect of oxidation on the IGC pattern. There does not seem to be too much effect on the lowest temperature transition although it may occur at a slightly higher temperature. The loss of water seems to occur at a significantly lower temperature. This is not surprising since the oxidized coal was heated in air at 100°C for 90 hrs. A vast majority of the water in this sample should be loosely held since it probably adhered to the surface of the coal after it was cooled. The major difference between the two coals is in the transition that should occur at higher temperatures. In the heavily oxidized sample there is almost no change in slope in this region indicating that the coal has probably not gone

fluid. There does appear to be some change occurring, which is a transient at approximately 330°C.

Overall IGC appears to be a very sensitive method for following the chemical and physical changes that occur when coals are heated in an inert atmosphere. Differences between coals of various ranks can be seen easily, as can the drastic effects of air oxidation.

Acknowledgments

The coal analysis were provided by I. Fox and P. C. Lindahl of the Argonne Analytical Chemistry Laboratory. The Bruceton coal was provided by J. W. Larsen of the Dept. of Chemistry, Lehigh University.

References

1. R. E. Winans, J. P. Goodman, P. H. Neill, and R. L. McBeth, ACS Fuel Chemistry Division Preprints, 30(4), 427 (1985).
2. S. G. Gilbert, in "Advances in Chromatography", Vol. 23, J. C. Giddings, E. Grushka, J. Cazes, and P. R. Brown, Eds., Marcel Dekker, New York (1984).
3. V. G. Berezkin, V. R. Alishoyev, and I. B. Nemirovskaya, J. Chromatography Library, 10, 197-223 (1977).
4. J. E. Guillet, in "New Developments in Gas Chromatography", J. H. Purnell, Ed., Wiley, New York, (1973).

TABLE 1. Composition of the Three Coals Studied.

Coal	% C (dmmf)	Empirical Formula
Upper Freeport mv Bituminous	89.0	C ₁₀₀ H ₇₀ N _{1.5} S _{0.5} O _{2.5}
Bruceton hvA Bituminous	82.3	C ₁₀₀ H ₇₈ N _{1.6} S _{0.3} O _{9.3}
Illinois No. 2 hvC Bituminous	73.4	C ₁₀₀ H ₈₇ N _{1.3} S _{0.8} O ₁₈

TABLE 2. Transition Temperatures for IGC Data Shown in Figure 1.

Sample	Temperature °C					
	T _A	T _B	T _C	T _D	T _E	T _F
Illinois No. 2 hvC	111	138	240	326	352	398
Bruceton hvA	110	130	230	341	368	429
Upper Freeport MV	115	158	248	360	370	430

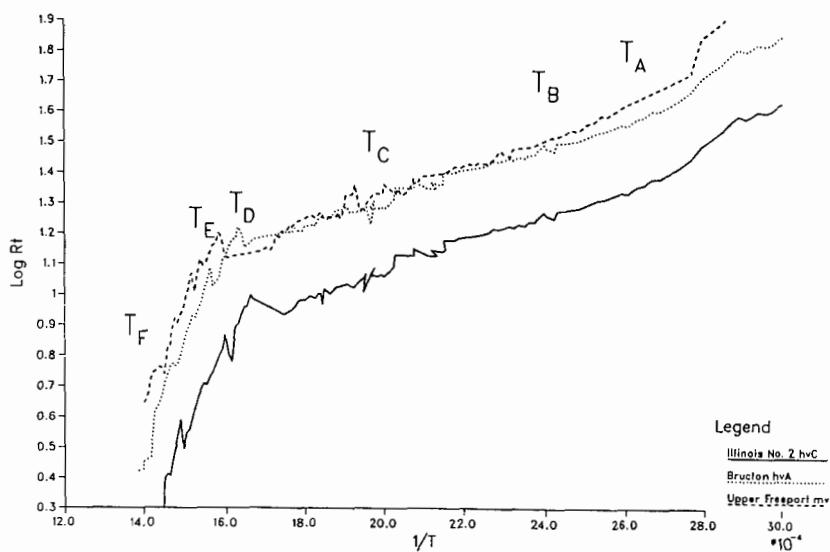


Figure 1. Data from inverse GC experiments. V_{ret} represents the retention volume; T is temperatures in $^{\circ}K$. Values for T_A - T_F are given in Table 2. — Illinois No. 2 hvC bituminous coal, Bruceton hvA bituminous coal, --- Upper Freeport mv bituminous coal.

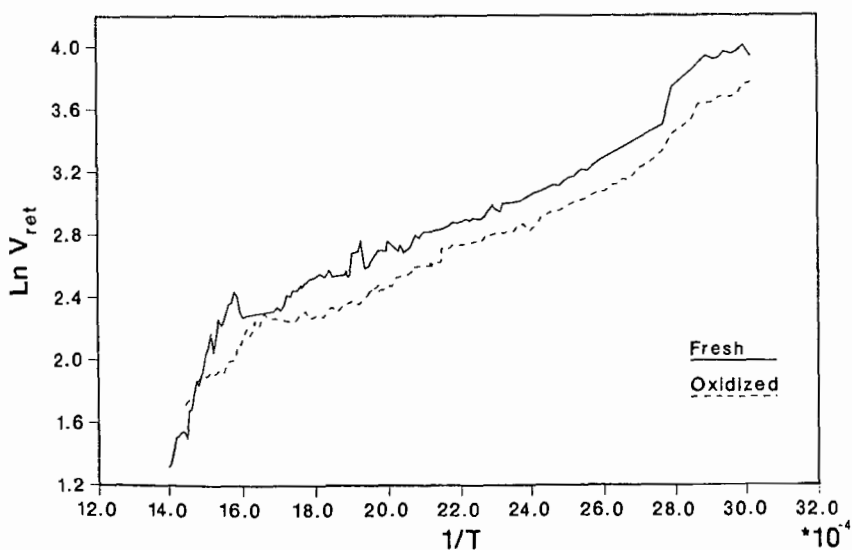


Figure 2. Comparison of data from an oxidized and a fresh sample of Upper Freeport mv bituminous coal.